

Neutron Diffraction Studies of Thermoelectric Materials

Bryan C. Chakoumakos, Brian C. Sales

David G. Mandrus

Solid State Division, ORNL

Veerle Keppens

National Center for Physical Acoustics

University of Mississippi

Oxford, Mississippi

Jeff W. Sharp, George S. Nolas

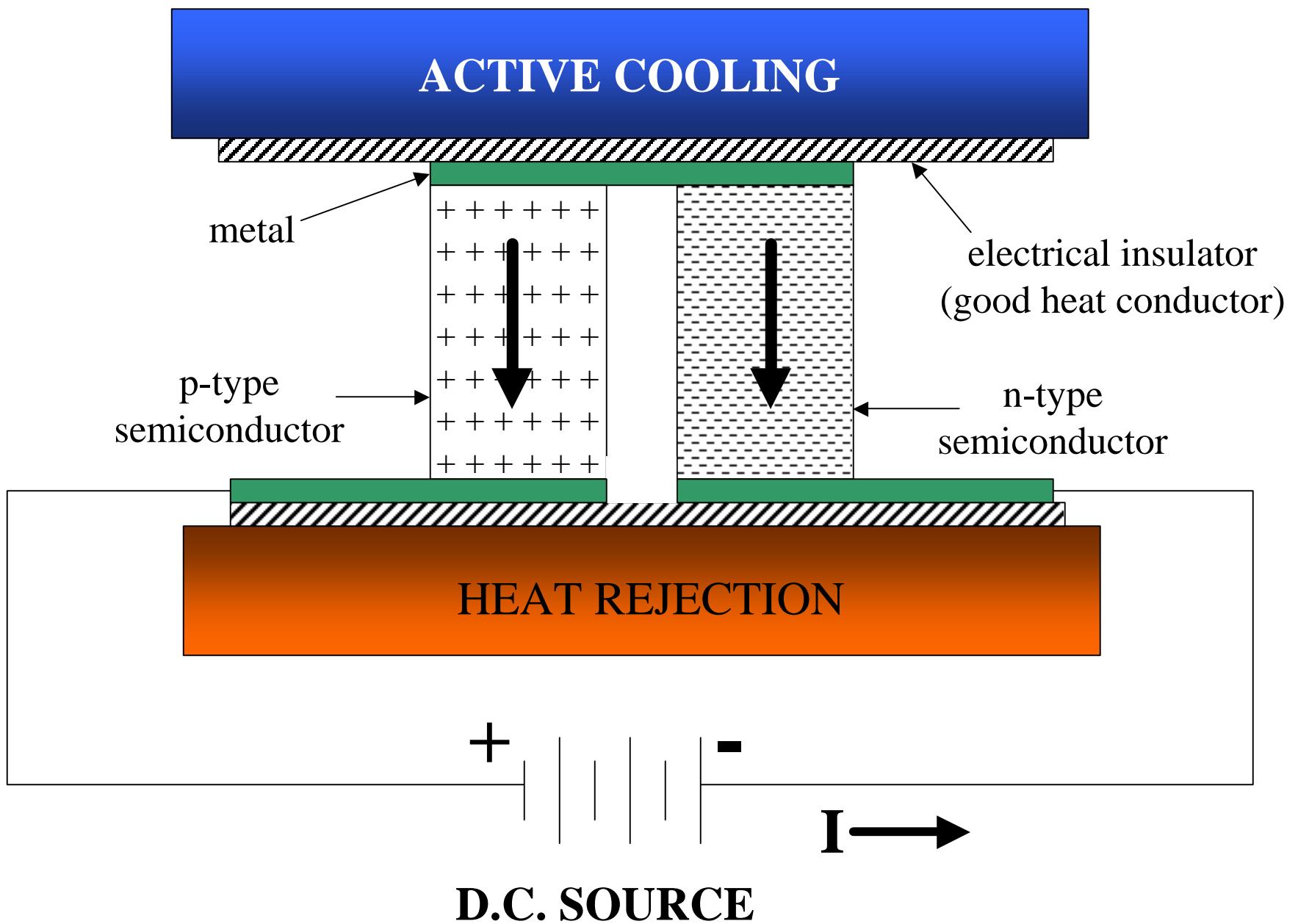
Marlow Industries Inc.

Dallas, Texas

Brief History of Thermoelectric Effects

- **1822, Thomas Seebeck**
 - electrical potential in the junction of two dissimilar metals when there is a temperature gradient, thermopower $S = V/\Delta T$
- **1834, Jean Peltier**
 - Passing current through two dissimilar conductors caused heat to be either emitted or absorbed at the junction, $dQ/dt = \Pi I$
- **1838, Heinrich Lenz**
 - demonstrates thermoelectric refrigeration
- **1931, Lars Onsager**
 - Proves $\Pi = (S_p - S_n)T$, posited by Lord Kelvin in 1854

THERMOELECTRIC COOLER



CURRENT AND *PROPOSED* APPLICATIONS FOR THERMOELECTRIC MATERIALS

- **REFRIGERATION**
 - Spot cooling of electronics
 - Infrared detectors
 - Computer central processing units
 - X-ray detectors
 - Fiber-optic laser packages
 - Picnic coolers (powered by car battery)
 - Air conditioning in submarines and railway coaches
 - *Water coolers*
 - *Superconducting electronics*
 - *Home refrigerators*

CURRENT AND *PROPOSED* APPLICATIONS FOR THERMOELECTRIC MATERIALS

- Power Generation
 - Deep-space probes (Pioneer, Viking, Voyager, Galileo)
 - Remote weather stations
 - Remote navigational systems
 - Submarines
 - Subsea power generation (for petroleum wellhead valves)
 - Conversion of waste heat into useful electrical power
 - *Large diesel trucks*
 - *Steel industry*
 - *Chemical industry*
 - Calorimetric sensors
 - *Continuous glucose monitoring in blood system*

Major drawback of thermoelectric refrigerators or power generators is their efficiency.

To improve the efficiency of thermoelectric devices one seeks larger values of the dimensionless figure of merit:

$$ZT = (S^2/kr)T$$

S = thermopower (Seebeck coefficient)

k = total thermal conductivity

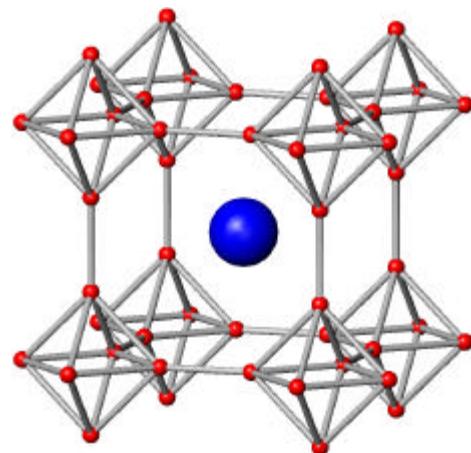
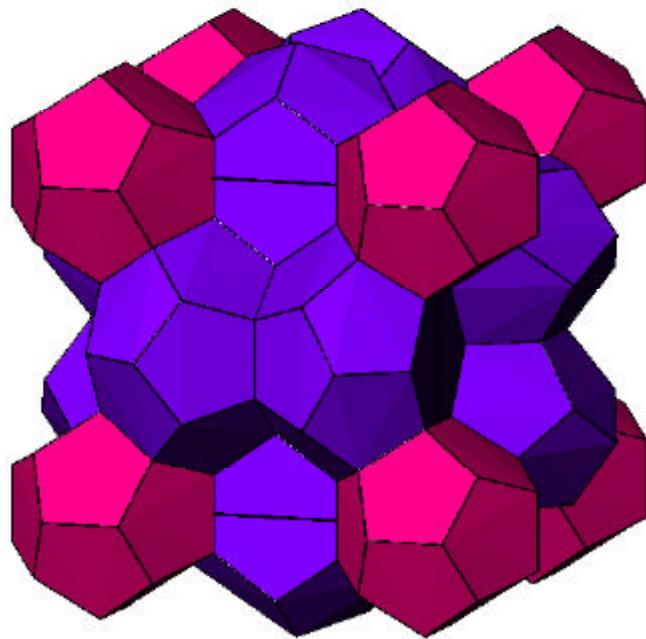
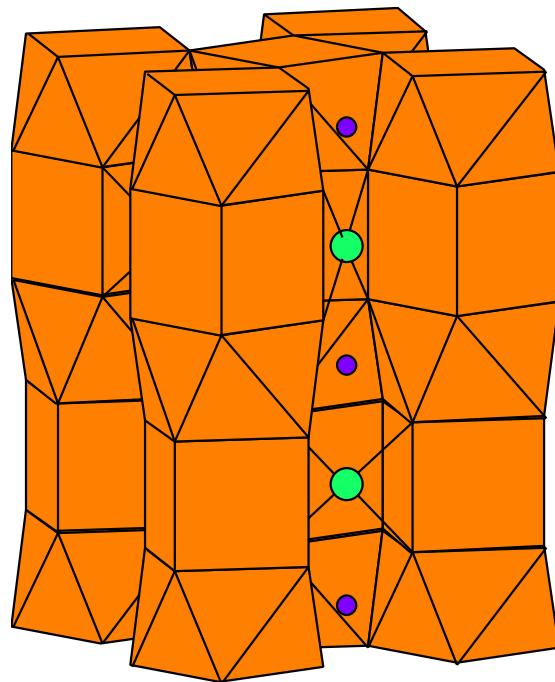
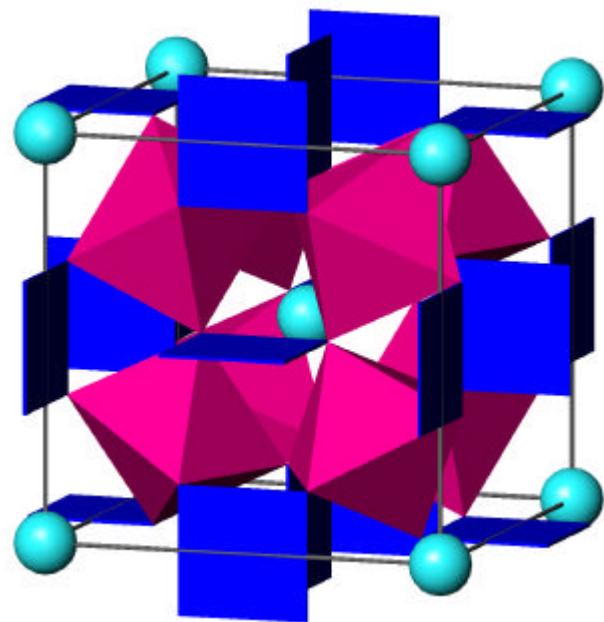
$$= k_{\text{lattice}} + k_{\text{electronic}}$$

r = electrical resistivity

All current thermoelectric devices use materials with $ZT = 1$.

PREMISE

The “electron crystal, phonon-glass” concept proposed by Slack (1995) is useful for improving thermoelectric performance.

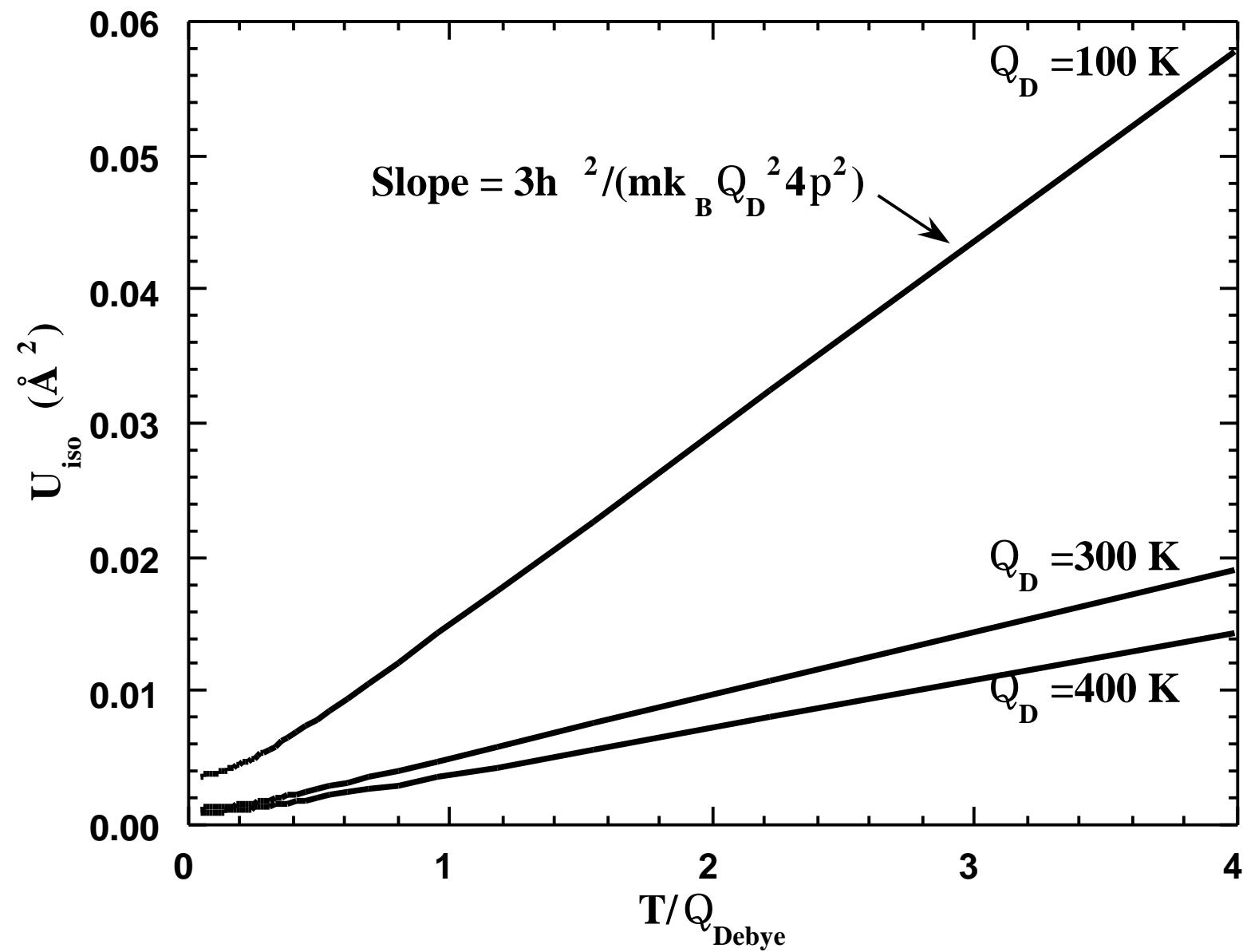


Structure - Property Relationships using ADP's

For clathrate-like semiconductors, the atomic displacement parameters determined from crystal structure refinement can be used to estimate the following quantities:

- Debye temperature
 - mean velocity of sound
 - Einstein frequency of “rattler”
 - heat capacity
-

- mean free path of the phonons
- lattice thermal conductivity



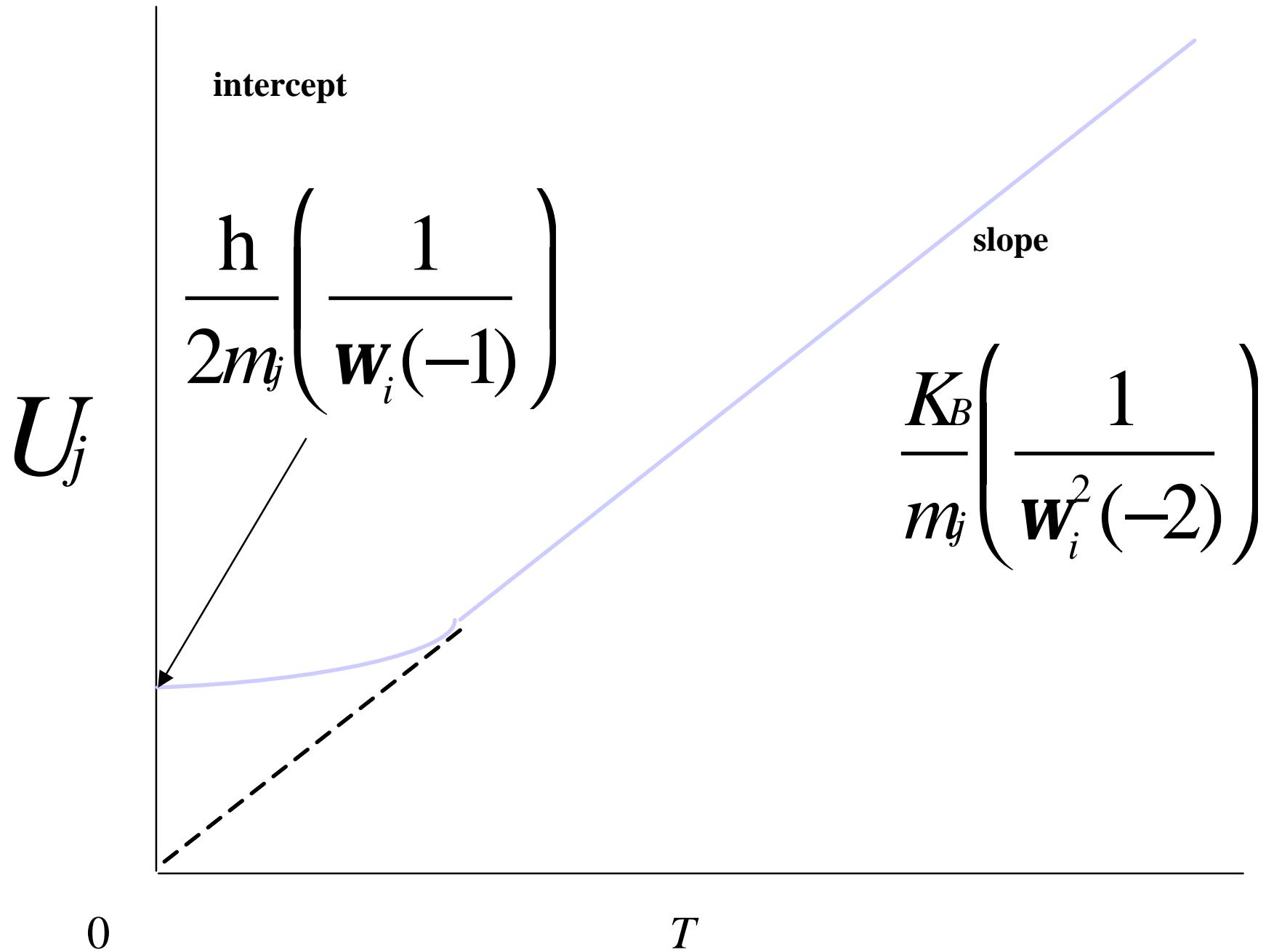
$$U_{iso} = \langle u^2 \rangle = \frac{3h^2}{4p^2 m k_B} \left[\Phi\left(\frac{\Theta_D}{T}\right) + 0.25 \left(\frac{\Theta_D}{T} \right) \right]$$

h = Planck constant

k_B = Boltzmann constant

F(x) = Debye integral

$$\Phi(x) = \frac{1}{x} \int \frac{y}{e^y - 1} dy$$



average velocity of sound

$$v_s = \frac{w_D}{K_D} = \frac{\Theta_D k_B 2p}{(6p^2 n)^{1/3} h}$$

n = number of atoms per unit volume

Einstein oscillator model

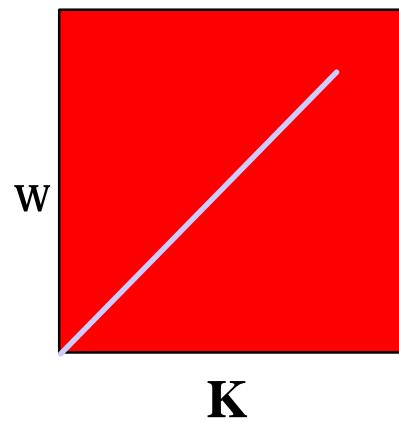
$$U_{iso} = \langle u^2 \rangle = \frac{h}{8p^2mv} \coth\left(\frac{hv}{2k_B T}\right)$$

at high T, $hn < 2k_B T$, so

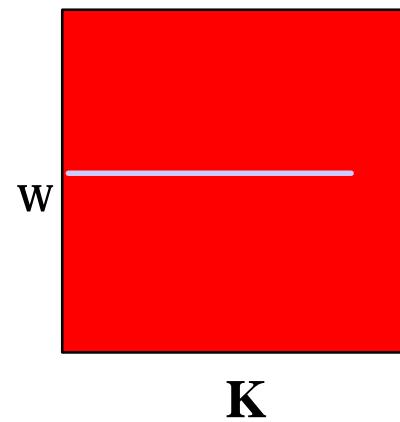
$$U_{iso} = \frac{k_B T}{K}$$

K = oscillator spring constant
 $= m(2\pi\nu)^2$

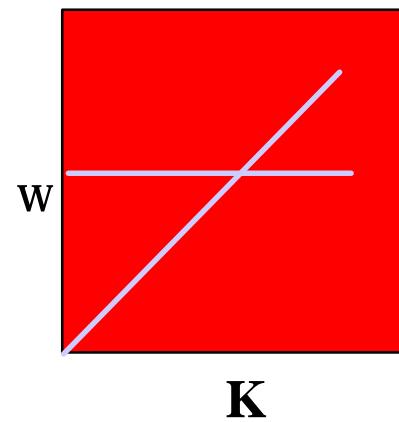
Debye



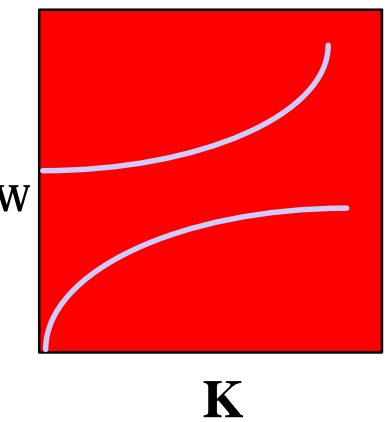
Einstein



Debye
+
Einstein



Reality
“Hybridized”



Heat Capacity

Einstein

$$C_V = 3Nk \left(\frac{h\mathbf{n}}{kT} \right)^2 \frac{\exp\left(\frac{h\mathbf{n}}{kT}\right)}{\left[\exp\left(\frac{h\mathbf{n}}{kT}\right) - 1\right]^2}$$

Debye

$$C_V = 9Nk \frac{T^3}{\Theta_D^3} \int_0^{\Theta_D/T} \frac{\exp(x)}{\left[\exp(x) - 1\right]^2} x^4 dx$$

Lattice thermal conductivity

$$k_{Lattice} = \frac{1}{3} C_V v_s d$$

C_V = heat capacity per unit volume

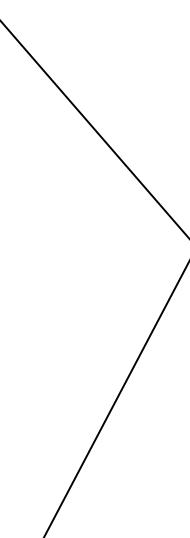
v_s = velocity of sound

d = mean free path of phonons

For d , we use the distance between the “rattlers”, which tend to dominate the scattering mechanisms.

Crystal structure refinement using neutron single-crystal diffraction data

- lattice dimensions
- atom positions
- site occupancies
- atomic displacement parameters
- magnetic structures



**as a function of:
composition,
temperature,
pressure**

Atomic Displacement Parameters

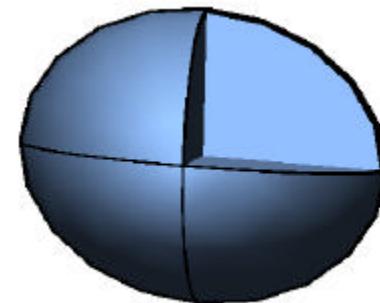
Isotropic

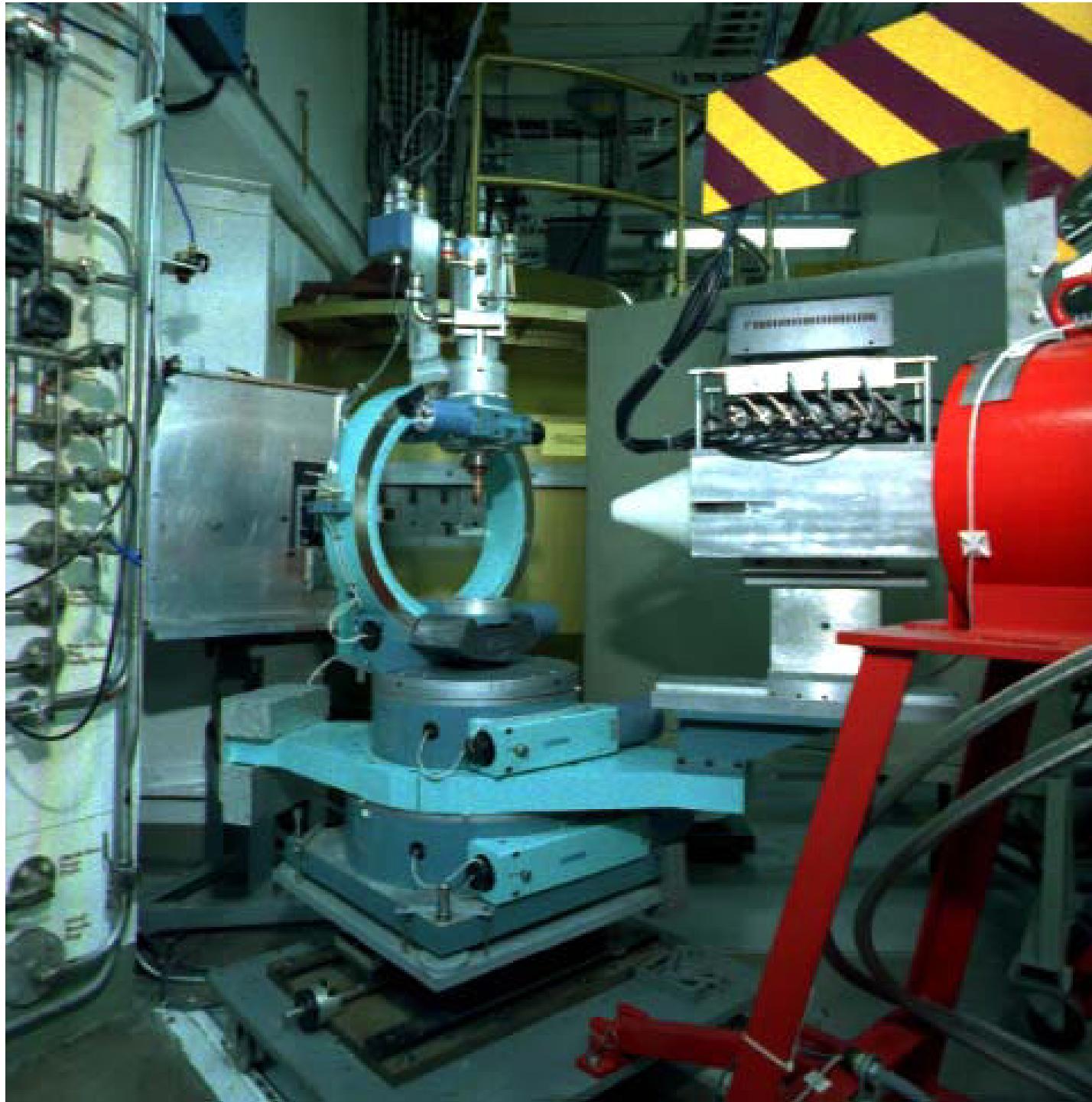
$$T' = \exp[-8p^2 U_{\text{iso}} \sin^2 Q/l^2]$$

Anisotropic

$$T' = \exp[-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* + 2u_{23}klb^*c^*)]$$

$$\begin{pmatrix} u_{11} & u_{12} & u_{13} \\ u_{12} & u_{22} & u_{23} \\ u_{13} & u_{23} & u_{33} \end{pmatrix}$$

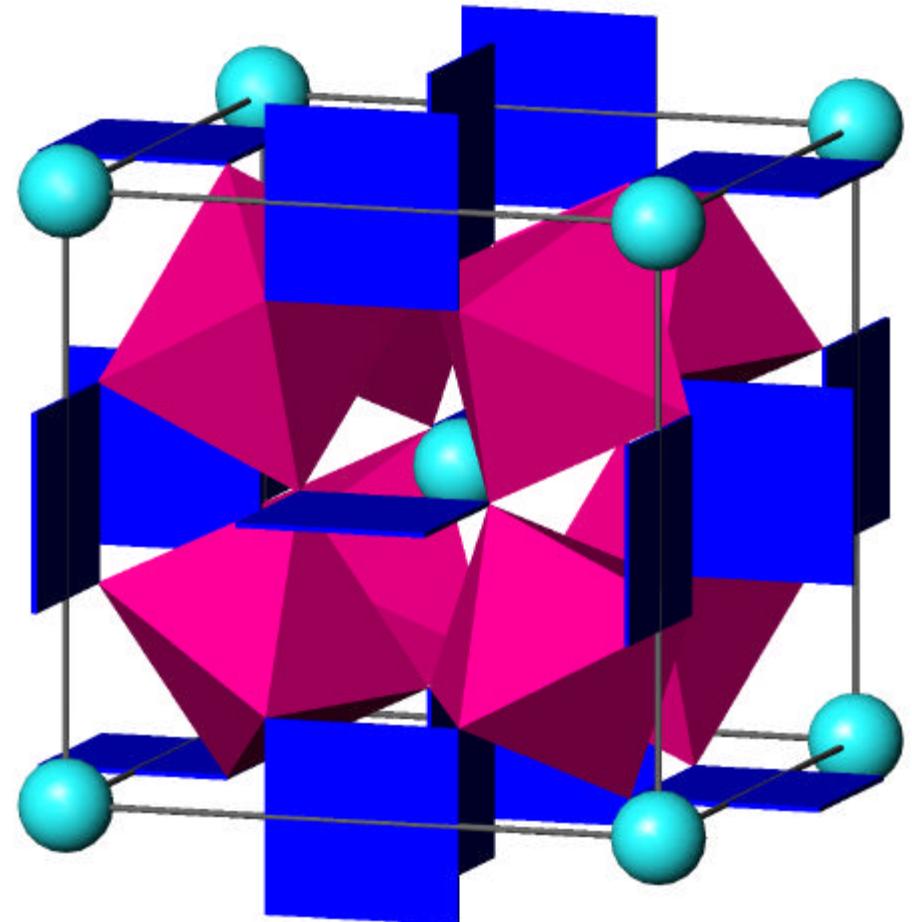


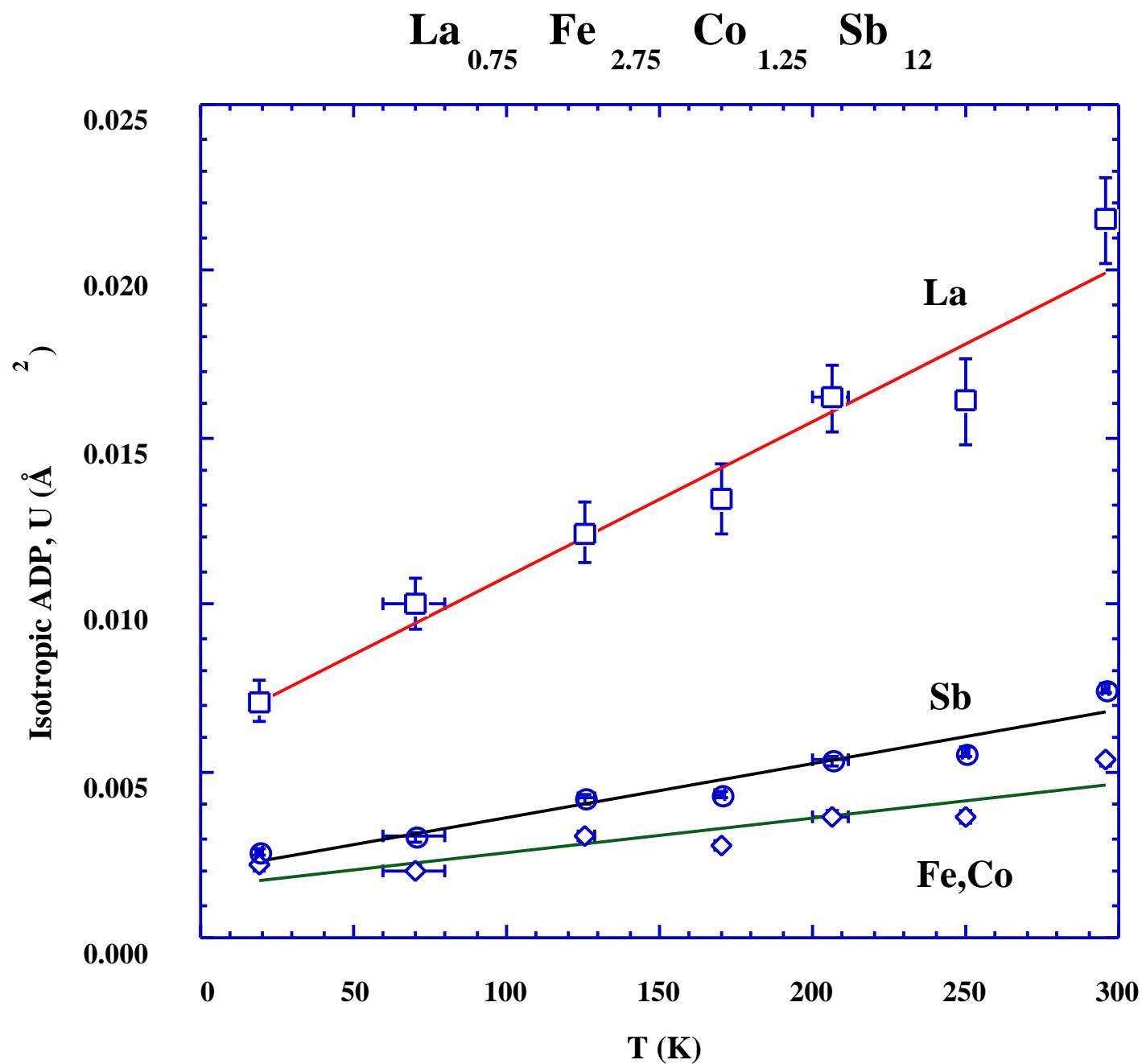


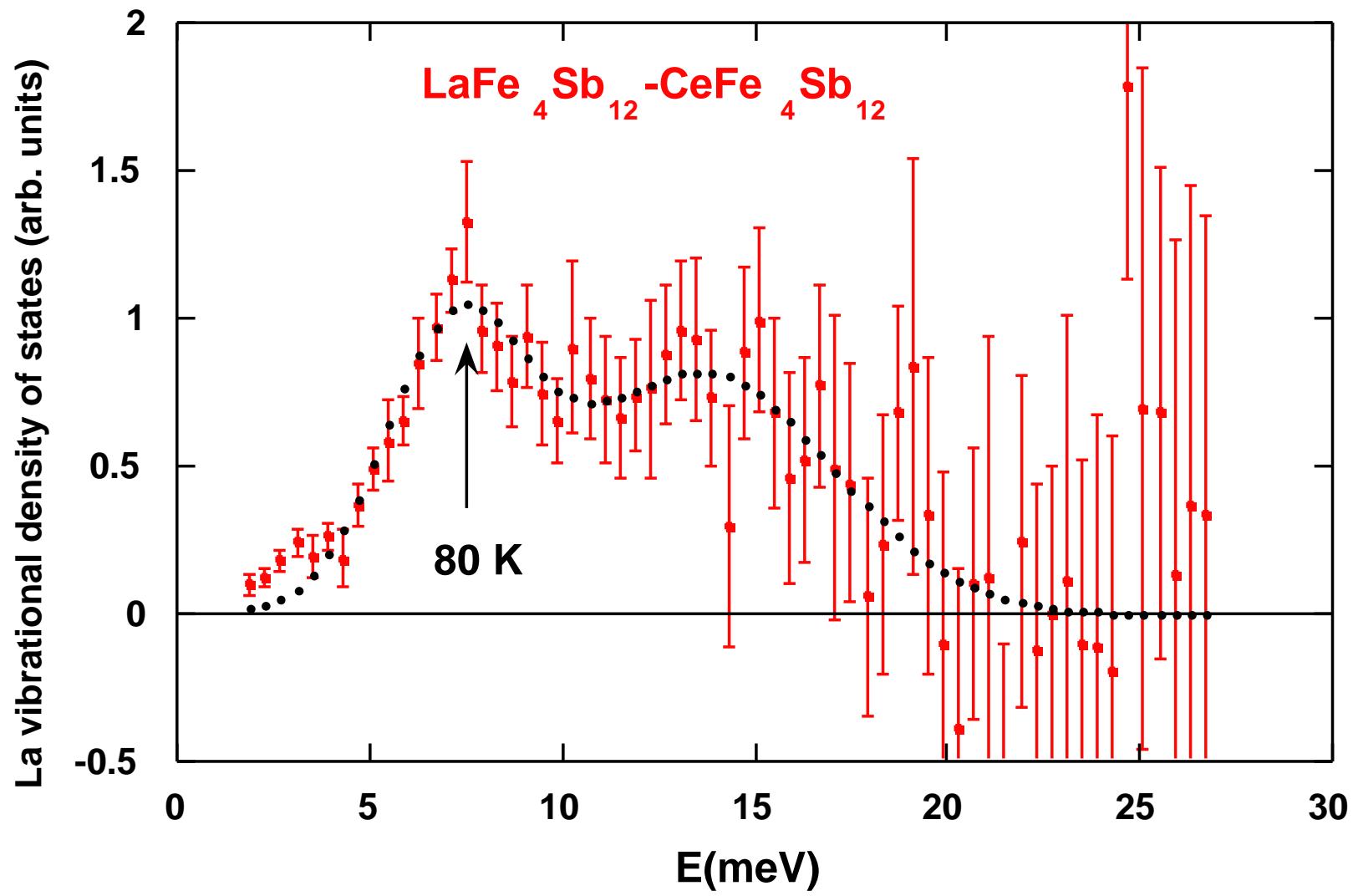
Filled Skutterudite Structure

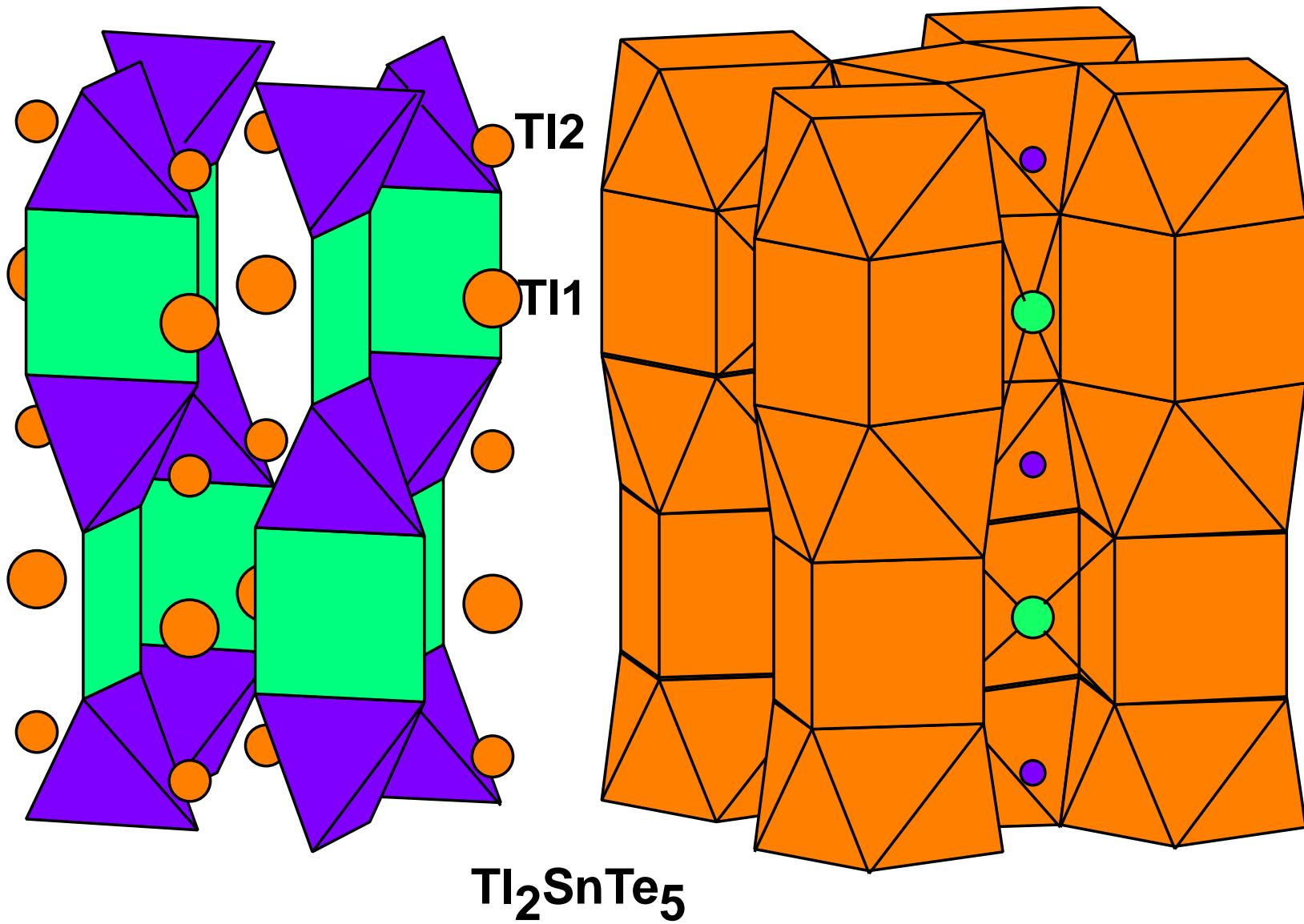
Jeitschko & Braun, *Acta Cryst. B* 33, 3401 (1977)

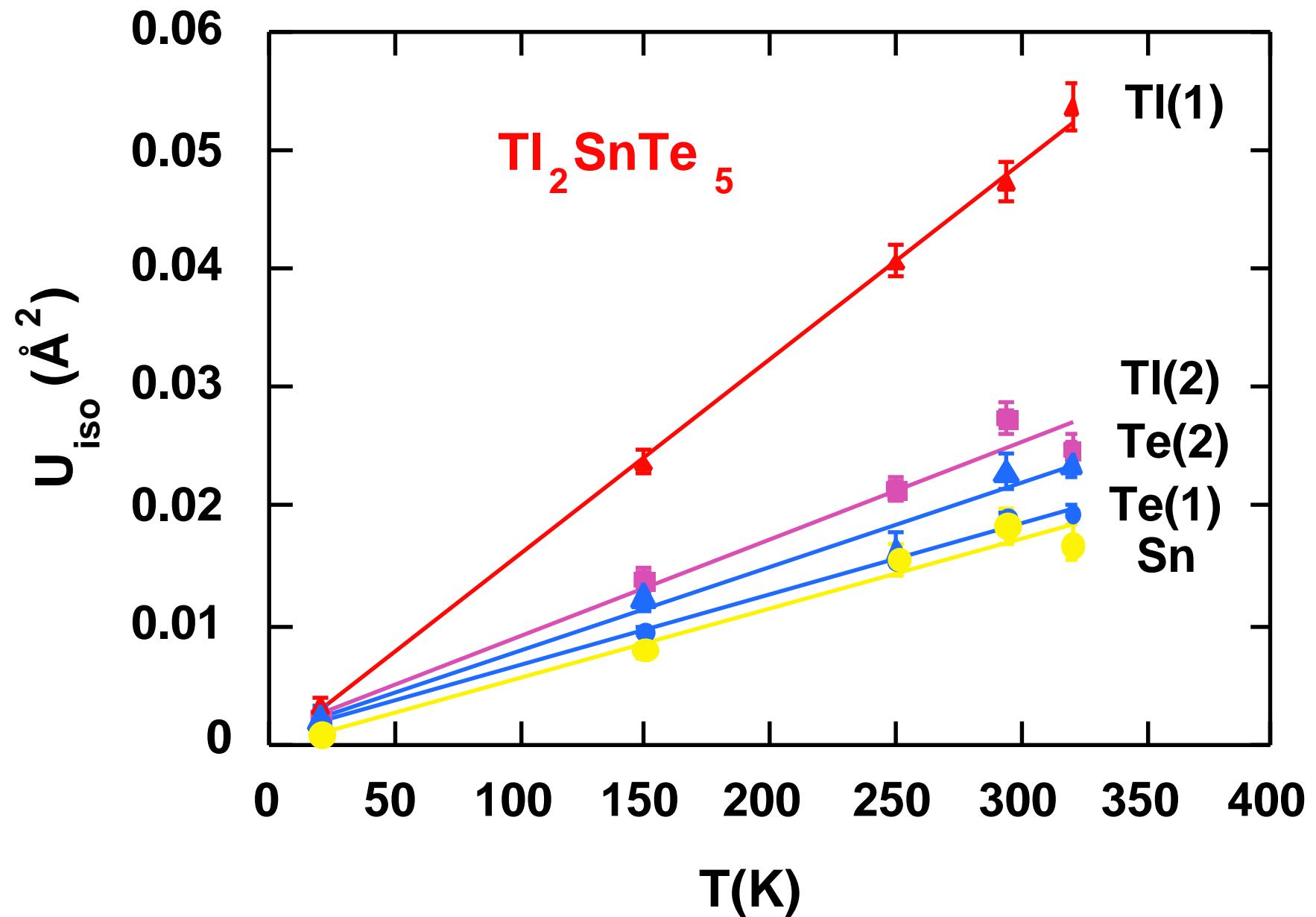
- AM_4Pn_{12}
 - $A=Ln, Ca, Sr, Ba, Th, U$
 - $M= Fe, Ru, Os, Co, Rh, Ir$
 - $Pn = P, As, Sb$
- > 60 end-members known
- cubic, $Im\bar{3}$, $a = 7.8-9.3 \text{ \AA}$
- electronic behavior:
 - superconductors
 - metals
 - semiconductors

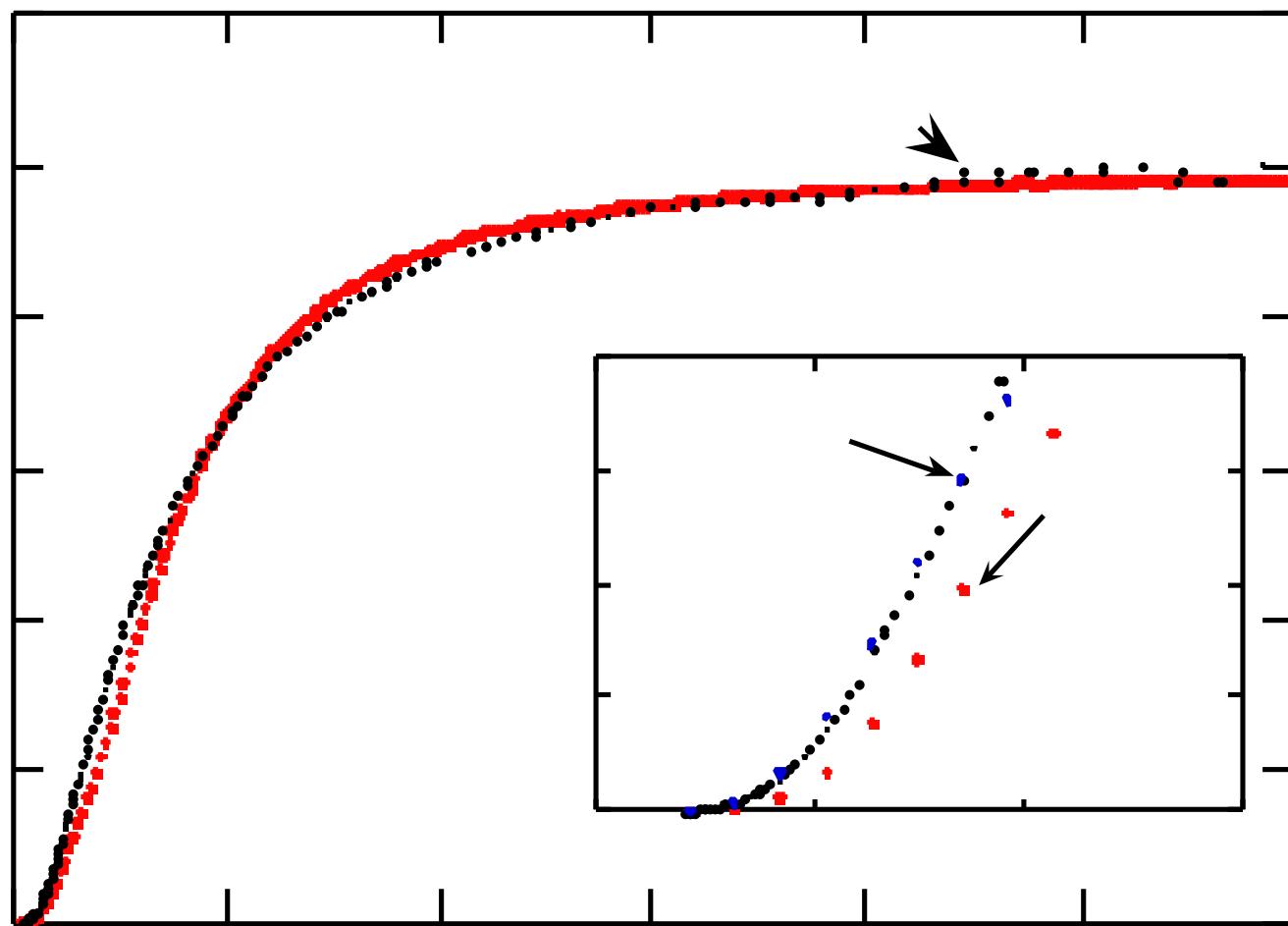




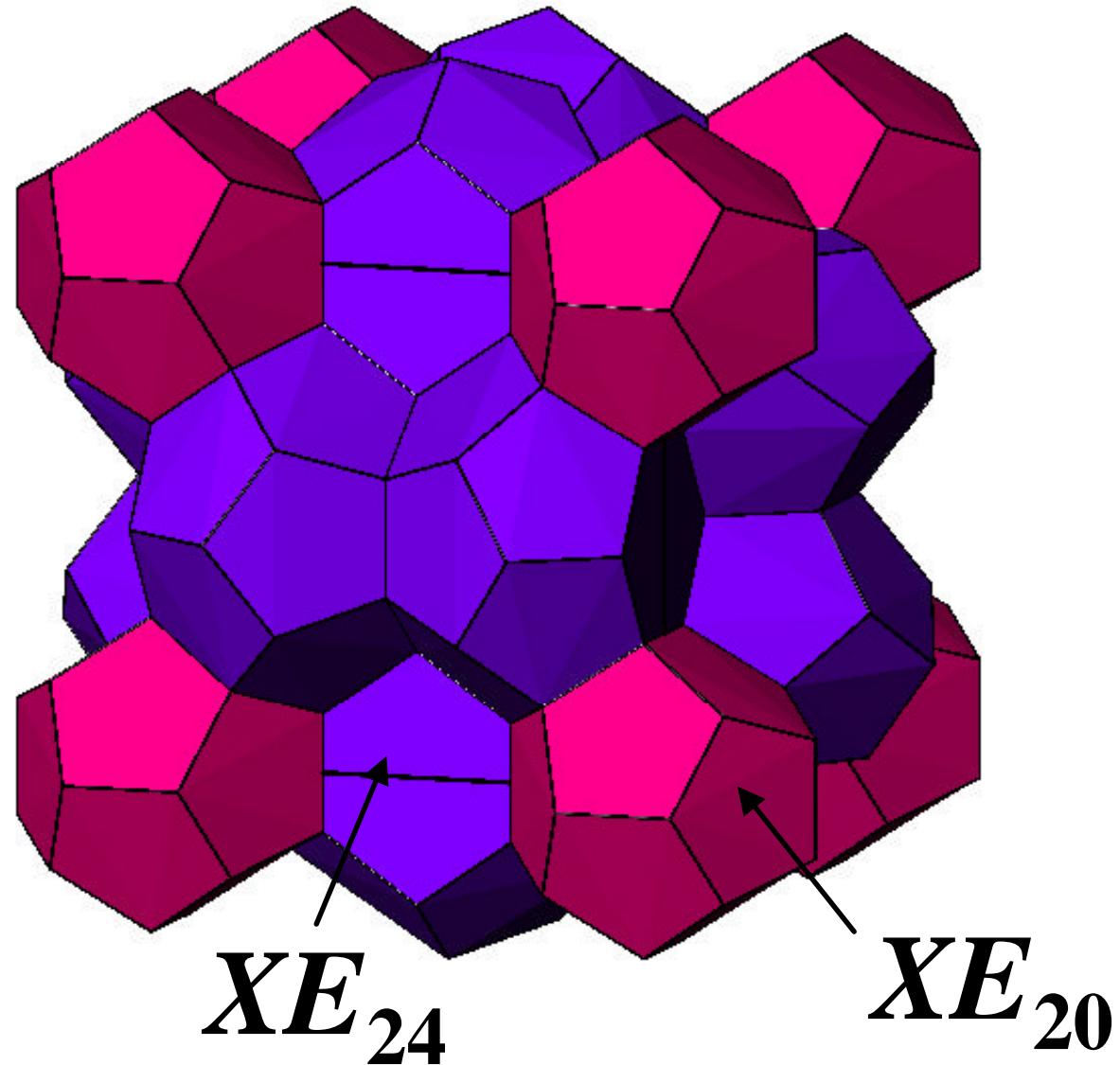


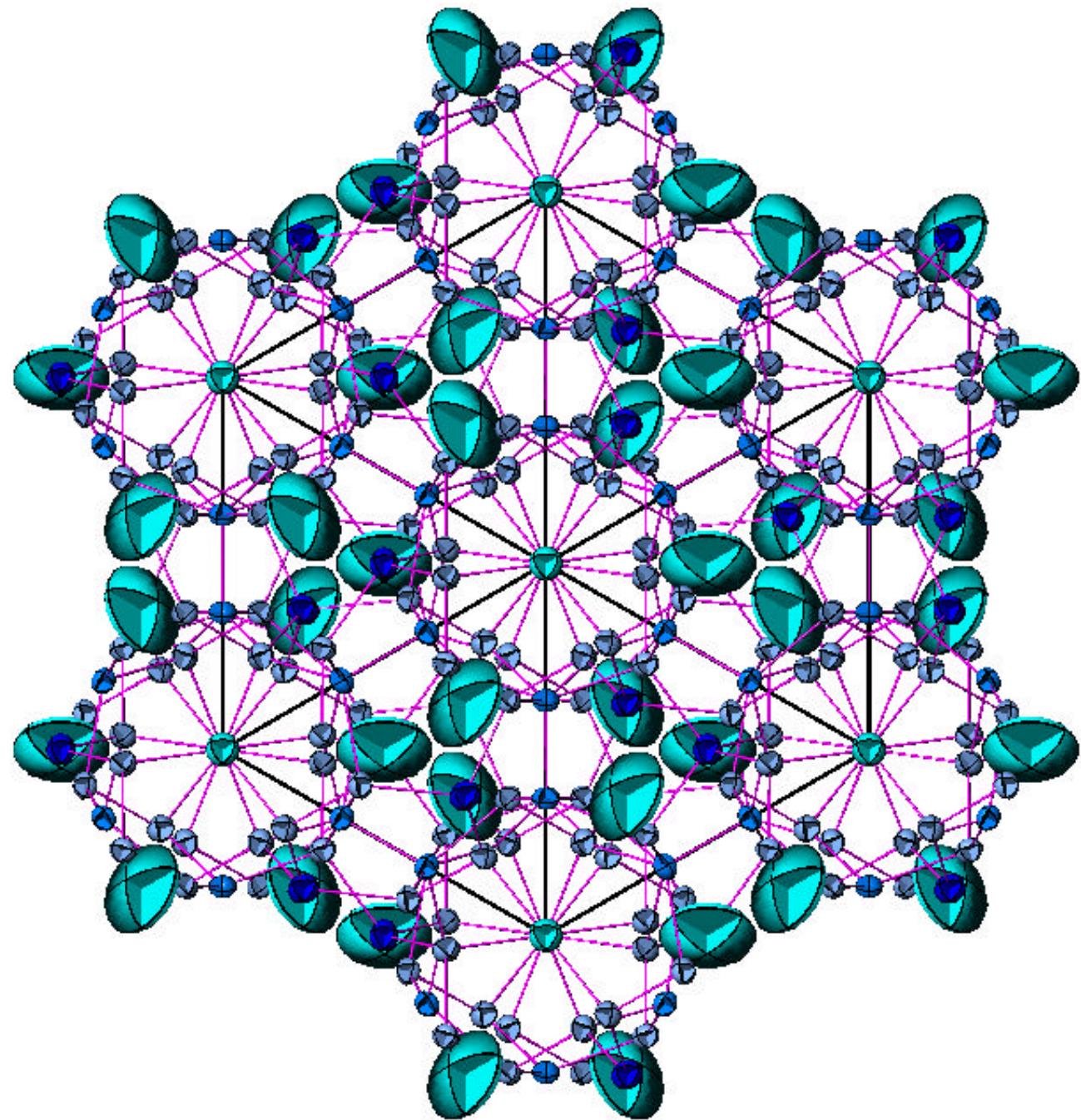




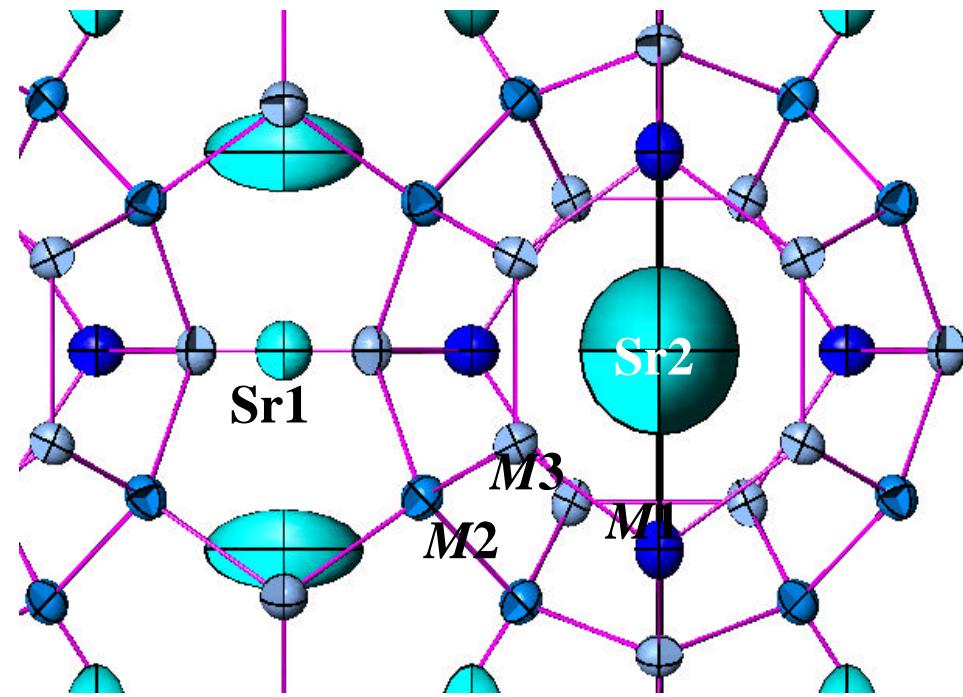


X_8E_{46} -structure type, $Pm\bar{3}n$,
 $X = \text{Na, K, Rb, Cs, Eu, Sr, Ba}; E = \text{Si, Ge, Sn, Al, Ga}$

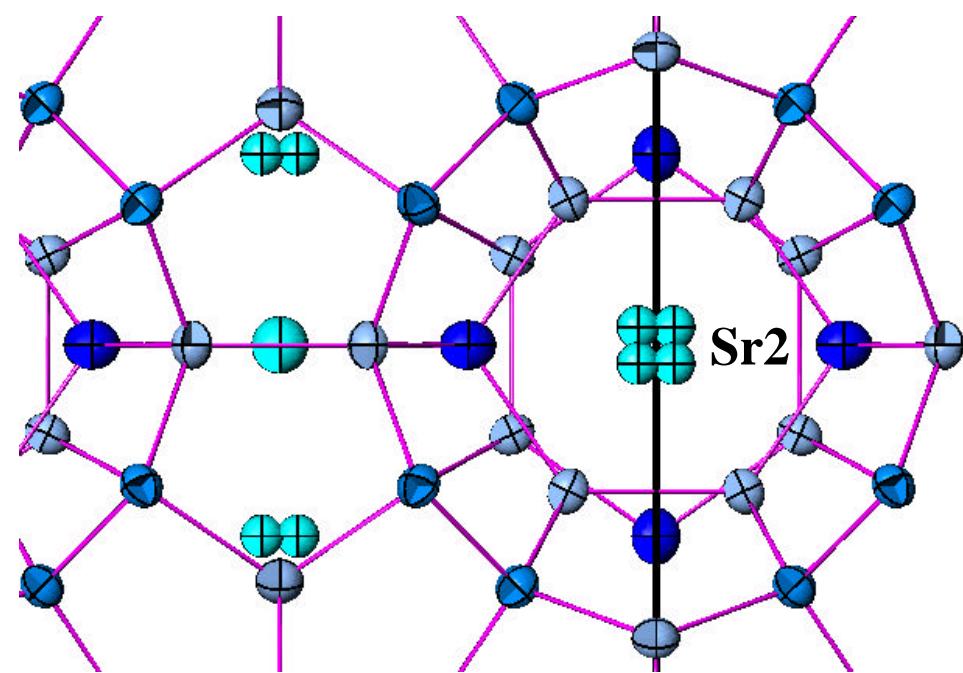


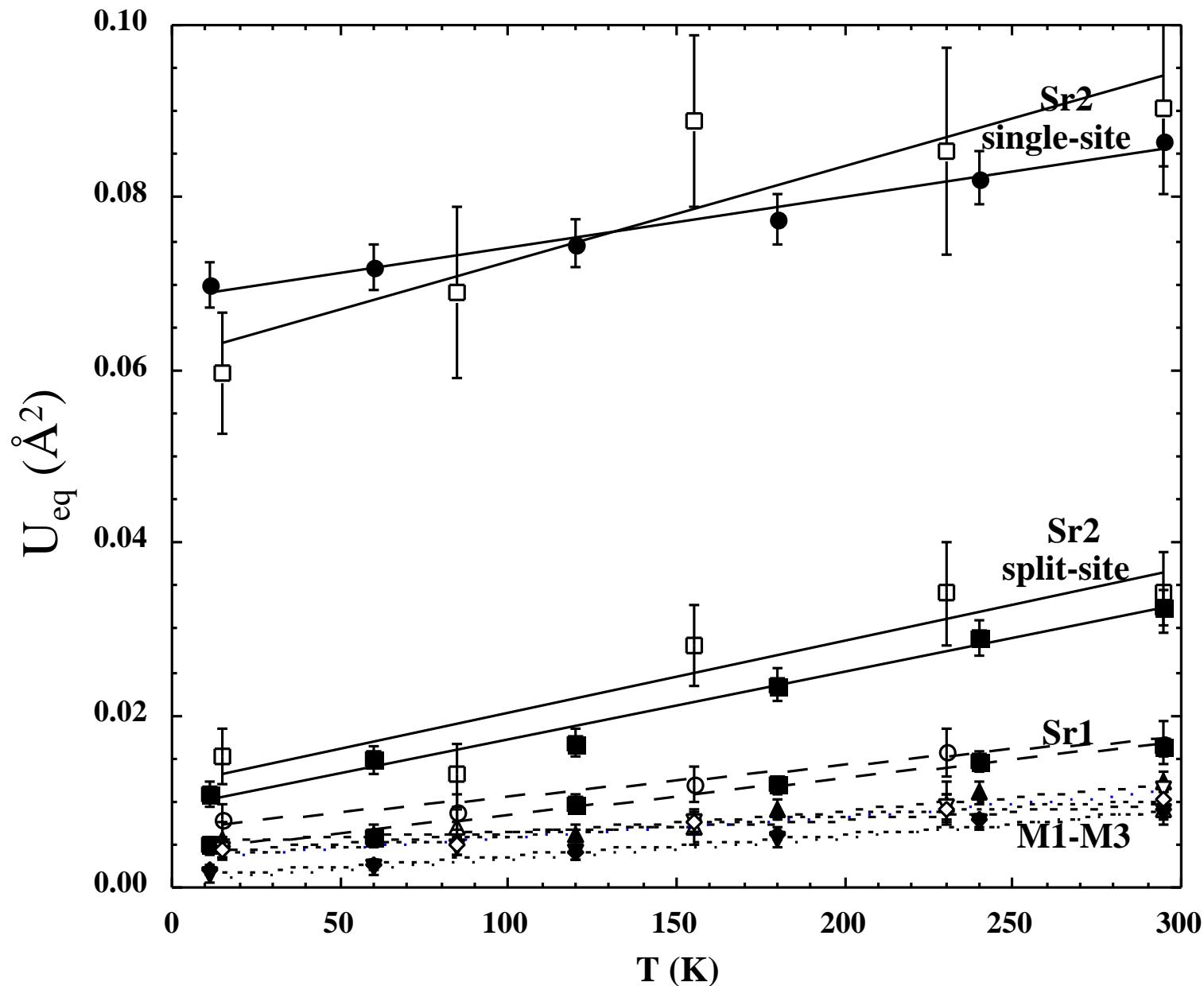


a.

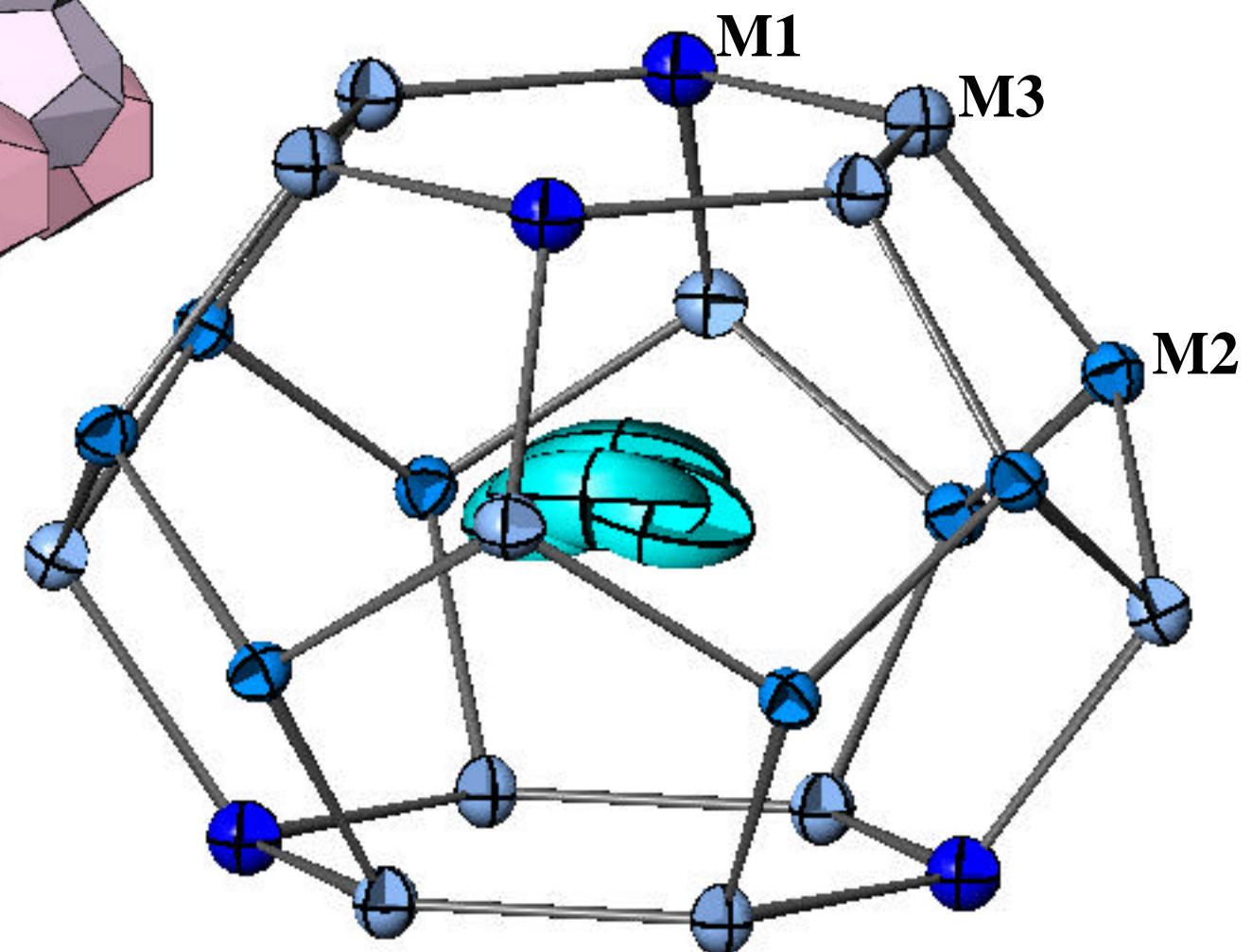
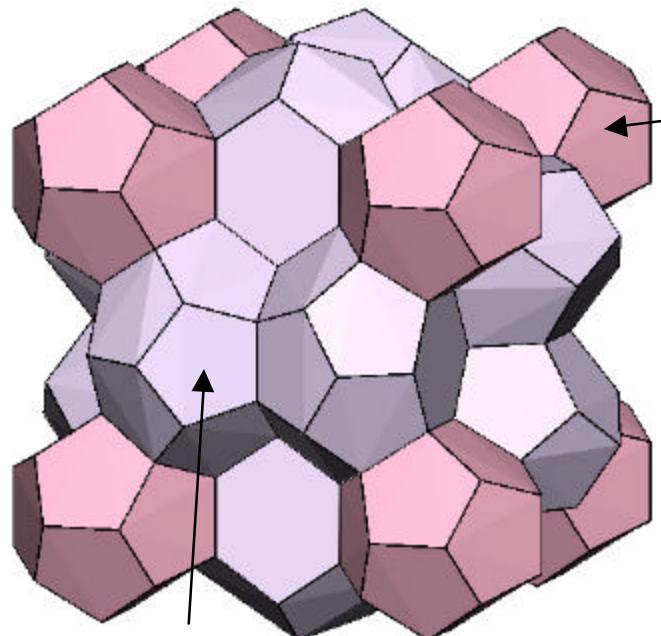


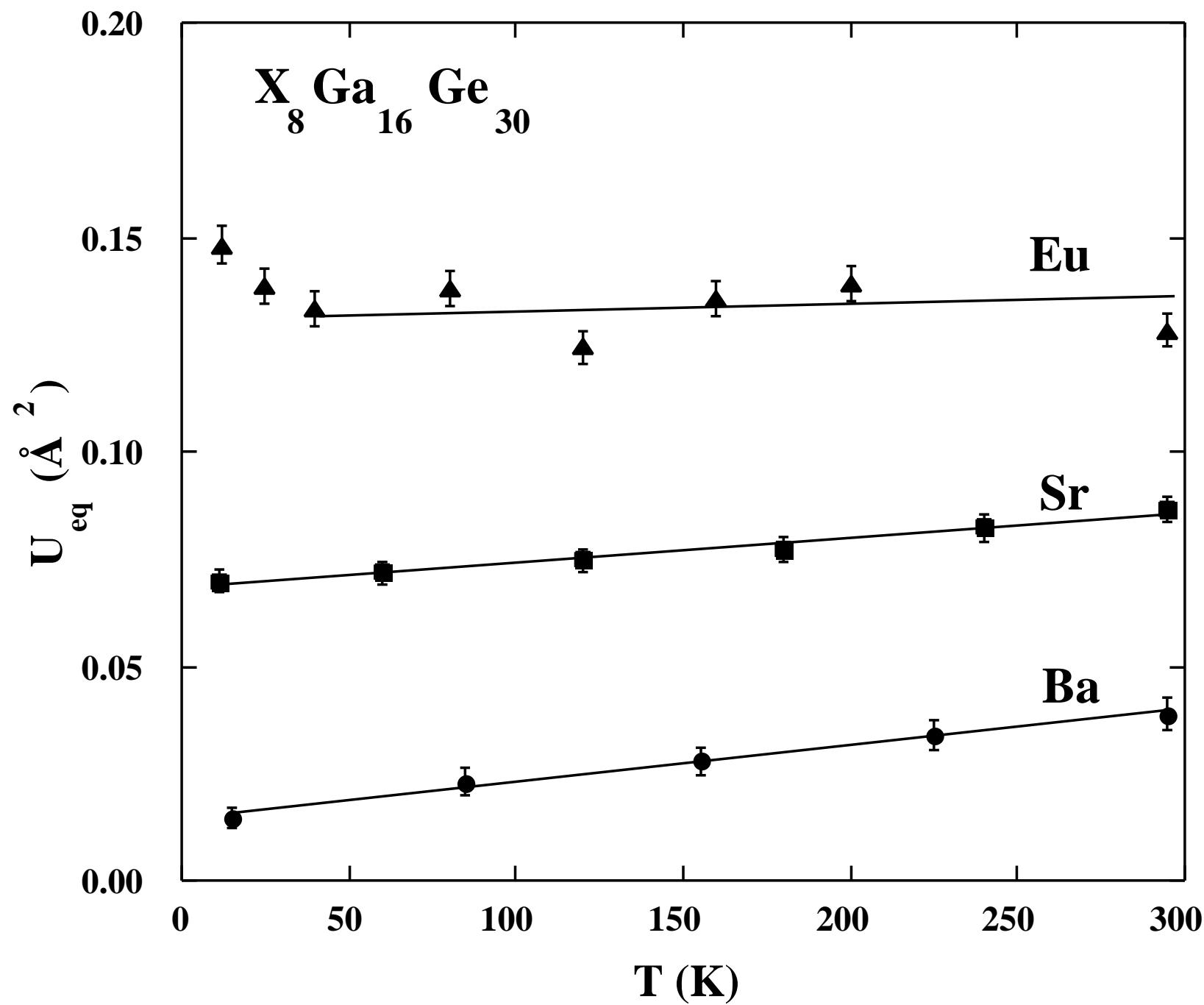
b.

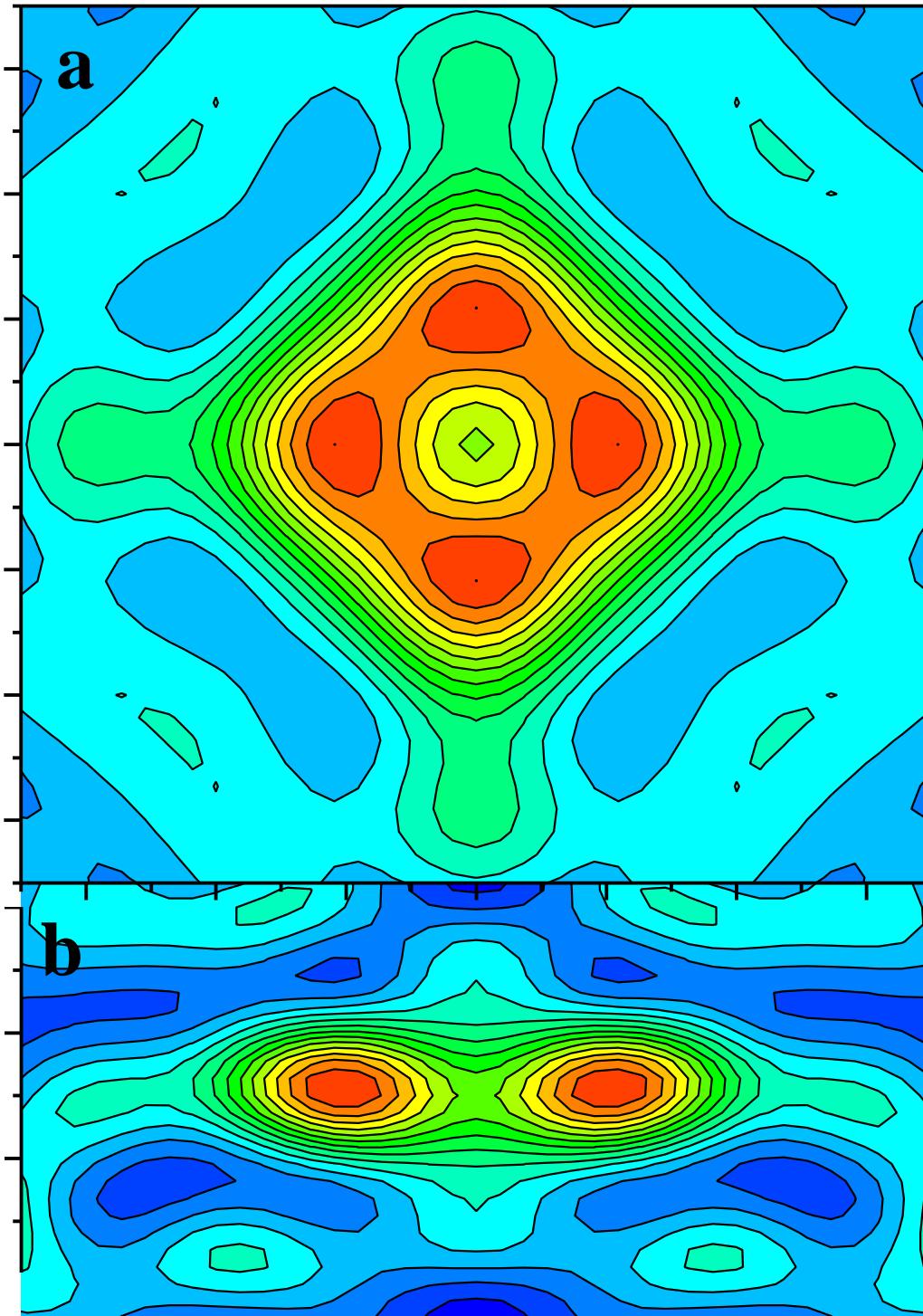




	LaFe ₄ Sb ₁₂		Tl ₂ SnTe ₅		Sr ₈ Ga ₁₆ Ge ₃₀	
	ADP ²⁰	Other	ADP ²¹	Other	ADP ⁸	Other
Θ_D (K)	299	305 ¹⁷	159	160 ⁶	274	300 ⁸
Θ_E (K)	79	80 ³	38	30 ⁶	72	87 ⁸
V _S (m/s)	2886	3007 ¹⁷	1488	--	2123	---
d (Å)	7.9	9	6.45	--	5.38	---
κ_L (W/cmK)	0.014	0.017 ¹⁷	0.0039	0.004 ⁶	0.007	0.009 ⁵

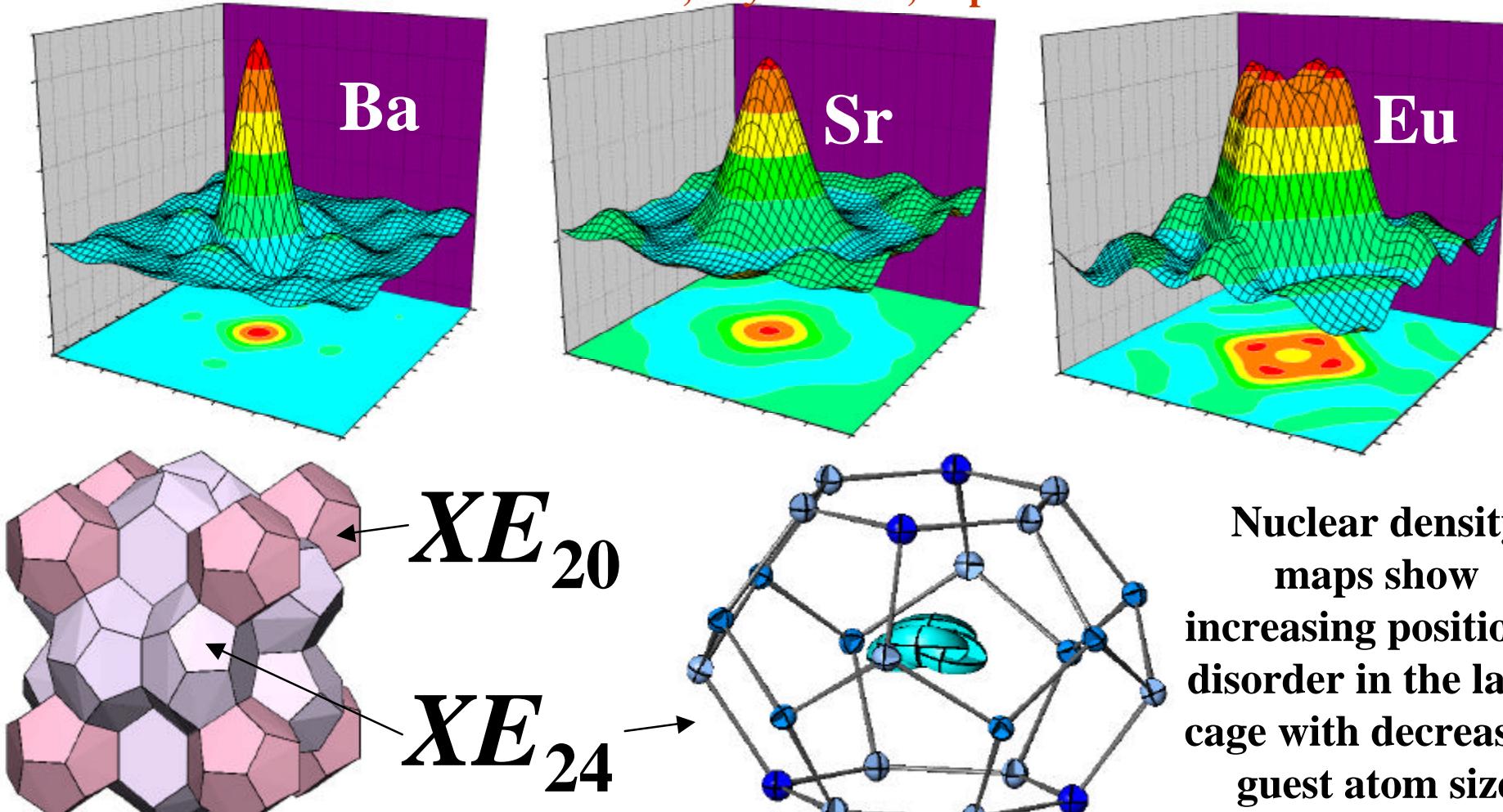


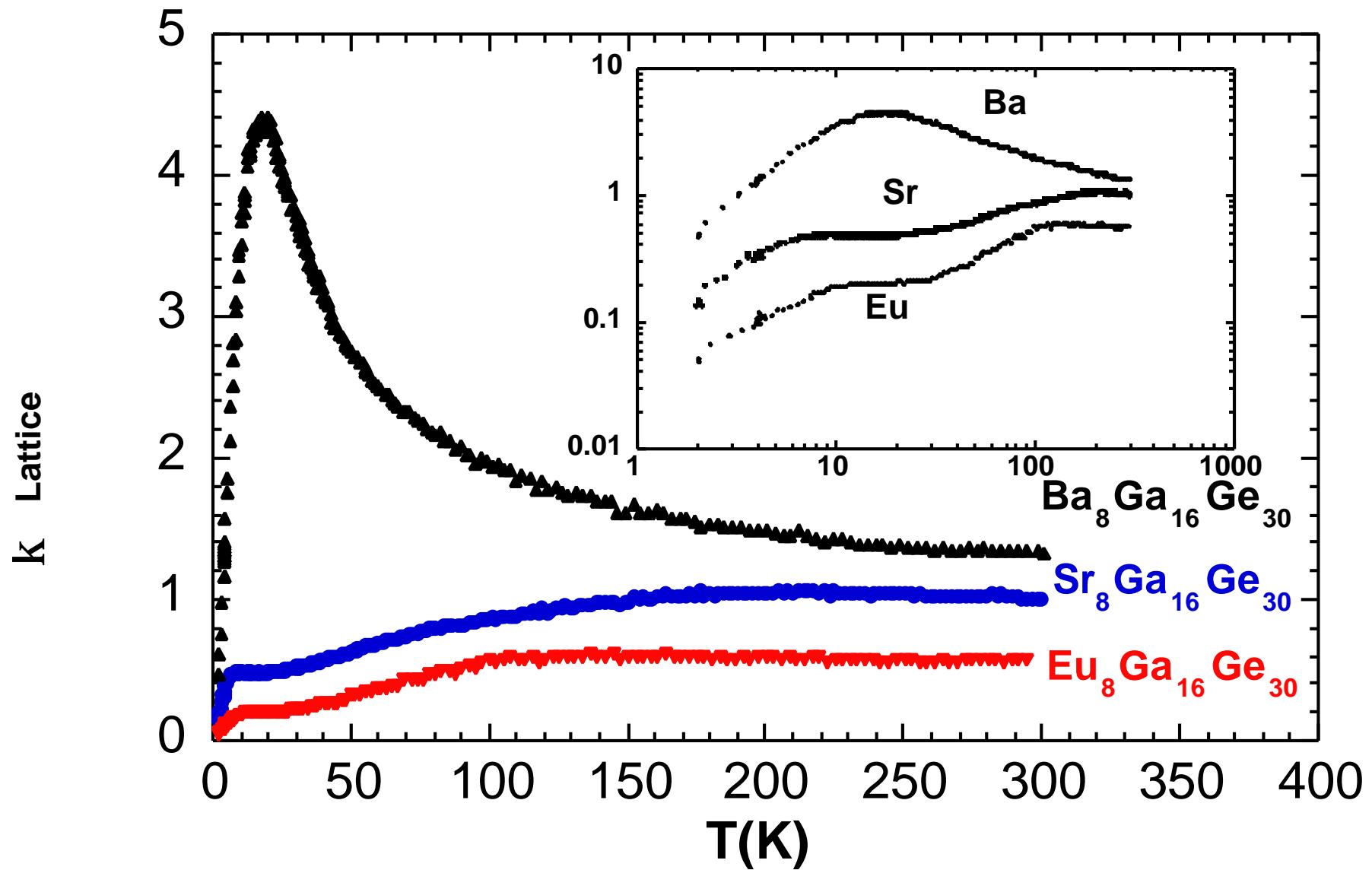




Neutron Crystallography Reveals Atomic Positional Disorder in the Clathrate-type $X_8\text{Ga}_{16}\text{Ge}_{30}$ ($X = \text{Ba}, \text{Sr}, \text{Eu}$) Thermoelectric Materials

Publications based on this work: Chakoumakos et al., *J. Alloys Comp.* 296 (2000) 80; Keppens et al., *Phil. Mag. Lett.* 80 (2000) 807; Chakoumakos et al., *J. Alloys Comp.*, in press; Sales et al., *Phys. Rev. B*, in press





Conclusions

- 👉 Atomic displacement parameters can be used to estimate lattice thermal conductivity. This structure - property relationship is aiding the search for new thermoelectric materials.
- 👉 The neutron crystallography reveals positional disorder of the cage occupants in clathrate-like semiconductors.